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- (71) Applicant (for all designated States except US): OWENS CORNING [US/US]; One Owens Coming Parkway, Toledo, OH 43659 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): RYND, Joseph, P. [US/US]; 3750 Silvercrest Drive, Stow, OH 44224 (US). LOH, Roland, R. [US/US]; 5181 Atterbury Lane, Stow, OH 44224 (US). BRIENDEL, Raymond, M. [US/US]; 3878 Edison Street Northeast, Hartville, OH 44632 (US).
- (74) Agents: GASAWAY, Maria, C. et al.; Owens Corning Science & Technology Center, 2790 Colombus Road, Bldg. 11-7, Granville, OH 43023-1200 (US).

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(54) Title: METHOD OF FORMING THERMOPLASTIC FOAMS USING NANO-PARTICLES TO CONTROL CELL MORPHOLOGY

(57) Abstract: A process for making closed-cell, alkenyl aromatic polymer foams using nano-particle nucleation agents to control the cell morphology of the resulting foam includes forming a polymer melt at a temperature above the polymer glass transition temperature (for crystal polymers) or the polymer melt point (for amorphous polymers); incorporating selected nano-particles into the polymer melt; incorporating blowing agents into the polymer melt at an elevated pressure; optionally incorporating other additives, such as flame retardants, into the polymer melt; and extruding the polymer melt under conditions sufficient to produce a foam product having a desired cell morphology, characterized by parameters such as reduced average cell size range and/or increased asymmetry of the cells.



METHOD OF FORMING THERMOPLASTIC FOAMS USING NANO-PARTICLES TO CONTROL CELL MORPHOLOGY

BACKGROUND OF THE INVENTION

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This invention relates to a process for making alkenyl aromatic polymer rigid foams having a wide range of cell morphologies by utilizing nano-particles as nucleating agents. Such rigid foams are useful for forming rigid insulating foam boards suitable in many conventional thermal insulation applications.

The physical properties of rigid polymer foam boards, such as their compressive strength, thermal conductivity, dimensional stability, water absorption rate, depend in large part on the micro-structure of the material forming the boards, that is, the cell morphology of the foam. However, it can be difficult to control polymer foaming to the degree necessary for consistent production of a desirable cell morphology that will tend to optimize the overall foam properties, or to improve a specific property, such as the thermal insulation value of the foam.

Prior art attempts to make foam micro-structures having desirable cell morphologies have included the use of nucleation agents such as powders formed from inorganic oxides, various organic materials and metals. Among these nucleation agents, the inorganic oxides, such as talc, titanium dioxide and kaolin, are the most commonly used. The size, shape, particle distribution and surface treatment of the nucleation agent(s) utilized to form a foam will all tend to affect the nucleation efficiency and, consequently, the cell size morphology and distribution in the resulting foam.

Conventional methods for controlling the cell morphology, however, tend to be limited by difficulties in evenly distributing particles of the nucleation agent throughout the polymer and/or suppressing coagulation of the dispersed particles. Certain structural defects in the resulting foams are generally attributed, at least in part, to dimensional differences between the particles of the nucleating agents — which may be in the range of several microns, particularly in situations where there has been some degree of coagulation — and the desired cell microstructures — which may have a target cell wall thickness of one micron or less — for a low density commercial insulation foams.

This size difference between the nucleation agent particles and the cell wall thickness may also result in relatively weak interactions between the nucleating agent and nano-scale polymer, thereby weakening the overall foam structure. Similarly, cell defects

may also be attributed, at least in part, to the hydrophilic surface of most conventional inorganic nucleation agents that makes them difficult to disperse evenly in a polymer. These effects tend to result in processing difficulties, such as corrugation of the resulting foam board, when nucleation agents are added at levels greater than about 2 weight percent or the median cell size of the resulting foam is less than around 120 microns.

Prior art attempts to avoid foam structure corrugation effects have utilized cell size enlarging agents such as the waxy compositions disclosed in U.S. Patent No. 4,229,396, and the non-waxy compositions disclosed in U.S. Patent No. 5,489,407.

Another effort directed toward foam structures having bi-modal cell morphology (Kanelite Super EIII, Kaneka, Japan) included use of immiscible blowing agents, such as water and hydrocarbon. This combination, however, tends to result in processing difficulties due to the low solubility of water in the polymer and the reaction of water with fire retardant, such as hexabromocyclododecane (HBCD) at the elevated temperatures typically utilized during the extrusion process.

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SUMMARY OF THE INVENTION

The present invention provides a process for making a closed-cell, alkenyl aromatic polymer foam in which nano-particle nucleation agents are utilized to control the cell morphology. The exemplary process comprises: 1) heating an alkenyl aromatic polymer to the temperature above the glass transition temperature of the polymer (for crystal polymer), or melt point of the polymer (for amorphous polymer) to form a polymer melt; 2) incorporating an appropriate amount of selected nano-particles into the polymer melt to alter the polymer property and process behavior, such as rheology, melt strength; 3) incorporating blowing agents into the polymer melt at elevated pressure; 4) incorporating other additives, such as flame retardants into the polymer melt; and 5) extruding and forming a foam board under an atmospheric or sub-atmospheric pressure (partial vacuum) to produce a desired cell morphology, characterized by parameters such as cell size range and distribution, cell orientation and cell wall thickness.

Further according to the present invention, the nano-particles are typically particles with at least one dimension less than 100 nm and may be incorporated into the polymers as surface modified nano-particles, nano-particles having mechnochemical bonds to a core micron sized particle, nano-particle compounds in combination with polymers, such as master batch compositions, and/or liquid blowing agents. Further, the nanoparticle

polymer compounds can be intercalated nano-layers, such as compounds formed simply by mixing nano-Montmorillonite (MMT) or expanded graphite with a polymer, or exfoliated nano-layers, such as compounds formed by the in-situ polymerization of polymer precursors in the presence of nano-MMT or other surface-modified inorganic or graphite particles.

A first exemplary embodiment of the present invention provides a process for making a rigid polymer foam having a relatively small median cell size of around 60 microns by using surface modified hydrophobic nano-MMT particles. Conventional foams, in comparison, tend to have a median cell size of more than 150 microns produced by using conventional inorganic nucleating agents such as hydrophilic talc. The rigid foams prepared according to this embodiment of the invention exhibited no detectable corrugation and an improvement in compressive strength of around 30%.

A second exemplary embodiment of the present invention provides a process for producing rigid foams having an increased cell orientation of at least about 1.4, compared with a conventional cell orientation of about 1.0, was observed by adding needle-shaped nano-particles of, for example, calcium carbonate, in addition to a conventional nucleating agent, such as talc.

A third exemplary embodiment of the present invention provides a process for forming an improved foam structure using a carbon dioxide blowing agent in combination with a nano-scale nucleating agent, such as nano-MMT, to produce a rigid foam having a reduced median cell size and thinner cell walls both to improve mechanical strength and decrease thermal conductivity (thereby increasing the insulation value) of the resulting foam.

25 BRIEF DESCRIPTION OF THE DRAWINGS

- FIG. 1 shows an SEM image of the cell wall structure of a typical XPS foam.
- FIG. 2 shows an SEM image of the cell strut structure of a typical extruded polystyrene ("XPS") foam.
- FIG. 3 shows an SEM image of an XPS foam with average cell size of about 81 microns produced with about 0.5% of a nano-clay nucleating agent.
 - FIG. 4 shows an optical microscope image of the cell size, cell size distribution, and cell orientation (x/z) of an XPS foam with 2% nano-calcium carbonate.

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FIG. 5 shows an optical microscope image of the cell size, cell size distribution, and cell orientation (x/z) of an XPS foam with 3.3% of a nano-expanded graphite nucleating agent.

FIG. 6 shows an SEM cell morphology image of an XPS foam sample prepared using 5% nano-MMT as a nucleating agent and 6% CO₂ as a blowing agent.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

The cell morphology includes parameters such as cell mean size, cell anisotropic ratio or cell orientation, cell density, cell size distribution, cell wall thickness, cell strut effective diameter, open/closed cell ratio, cell shape, such as pentagonal dodecahedral, rhombic dodecahedron, tetra dodecahedral (with curved surface), and other models of cells such as bi-cell and cell-in-cell models. Within these cell morphology parameters, cell mean size, cell wall thickness, cell strut effective diameter, and cell orientation are the key parameters for determining the foam physical properties of closed cell foams. FIGS. 1 and 2 show the SEM imagines of the cell wall and strut structure of a typical XPS foam. If a polymer foam is ideally depicted as a close wall of pentagonal dodecahedral cells in a uniform size, the cell wall thickness and the strut effective diameter then depend primarily on the density of the foam and the cell size.

This invention uses nano-particles and a related extrusion process for controlling the cell size, cell wall thickness, strut effective diameter, as well as cell orientation within a relatively broad range. Although conventional polymer foams tend to exhibit a cell mean size in the range between about 120 and 280 microns. By utilizing the nano-particle technology according to the present invention, it is possible to manufacture polymer foam structures having a cell mean size from several tens of microns to several hundred microns. The nano-particles utilized in manufacturing polymer foams according to the present invention are preferably included in the polymer melt at a rate of between about 0.01 to about 10 weight %, or, more preferably, from about 0.05 to about 2.5 weight % of the alkenyl aromatic polymer material.

The particle size of the present nano-particle cell size controlling agent is typically no greater than 100 angstroms in at least one dimension, and may be an organic or inorganic material either with or without surface modification. The primary component of the foam structure is an alkenyl aromatic polymer material. Suitable alkenyl aromatic

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polymer materials include alkenyl aromatic homopolymers and copolymers of alkenyl aromatic compounds and copolymerizable ethylenically unsaturated comonomers.

The alkenyl aromatic polymer material may further include minor proportions of non-alkenyl aromatic polymers. The alkenyl aromatic polymer material may be comprised solely of one or more alkenyl aromatic homopolymers, one or more of each of alkenyl aromatic homopolymers and copolymers, or blends of any of the foregoing with a non-alkenyl aromatic polymer. Suitable alkenyl aromatic polymers include those derived from alkenyl aromatic compounds such as styrene, alpha-methylstyrene, chlorostyrene, bromostyrene, ethylstyrene, vinyl benzene, and vinyl toluene. A preferred alkenyl aromatic polymer is at least 95% polystyrene and may be composed completely of polystyrene.

The present foam structure will also typically include one or more blowing agents selected from 1) organic blowing agents, such as aliphatic hydrocarbons having 1-9 carbon atoms (including, for example, methane, ethanol, ethane, propane, n-butane and isopentane) and fully or partially halogenated aliphatic hydrocarbons having 1-4 carbon atoms (fluorocarbons, chlorocarbons and chlorofluorocarbons); 2) inorganic blowing agents, such as carbon dioxide, nitrogen and water; and 3) chemical blowing agents, such as azodicarbonamide, p-toluenesulfonyl. Useful blowing agents include 1-chloro-1,1-difluorocthane (HCFC-142b), HCFC-134a, carbon dioxide, blends of HCFC-142b with carbon dioxide, HCFC-134a with carbon dioxide, carbon dioxide with ethanol, or carbon dioxide with water. The foam composition may also incorporate various additives, such as flame retardants, mold release aids, pigments and fillers, intended to improve the processing of the foam or modify one or more properties of the resulting foam.

Exemplary embodiments of polymer foam manufactured according to the present invention can exhibit densities of from about 10 to about 500 kg/m³, but will more preferably have densities of from about 20 to about 60 kg/m³ when measured according to ASTM D-1622. Although the polymer foams manufactured according to the present invention may have structures exhibiting both closed cells and open cells, preferred foam compositions will have at least 90 percent closed cells as measured according to ASTM D2856-A.

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The following are examples of the present invention, and are not to be construed as limiting. Unless otherwise indicated, all percentages, parts, or proportions are based on weight of the total composition.

5 EXAMPLES

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A series of exemplary and comparative foam structures were prepared and evaluated to determine cell morphology, that is, cell size, cell wall thickness (FIG. 1), effective diameter of cell strut (FIG. 2), cell anisotropy ratio, and certain other properties related to the foam cell morphology.

The physical properties tested included one or more of density, compressive strength, thermal conductivity, aged thermal insulation value, thermal dimensional stability. In connection with these examples, cell size was measured according to ASTM D3576; density was measured according to ASTM D1622; thermal conductivity was measured according to ASTM D1621; and thermal dimensional stability was measured according to ASTM D1621; and thermal dimensional stability was measured according to ASTM D2126.

The foam structures were made with a twin co-rotated screw extruder comprising a pair of extruder screw, a heating zone mixer, a blowing agent injector, a cooler, a die and a shaper in accord with the operational conditions listed below in Table 1. Unless otherwise indicated, the polymer utilized in preparing the example foam compositions was an AtoFina granular polystyrene having a weight average molecular weight (M_w) of about 250,000, and melt index of about 3.1 gm per 10 minutes.

Table 1

	LMP Co- rotating Twin Screw Extruder with Static Cooler	Leistritz MIC 27 GL/400 Co-rotating Twin Screw Extruder
Die /Shaper	Flat face die/Shaper plate	20 x 2 mm Flat Slot Die
Forming Atmosphere	Atmosphere/Vacuum	Atmosphere
Throughput kg/hr.	100 – 200	6 - 10
Wt.% of HCFC-142b	10.5 - 11.5	
Wt.% of HCFC-142b/22		
Wt.% of CO ₂	•	-
Mixing Temperature - °C	210-230	200 - 220
Extruder Pressure - kPa (psi)	13000 - 17000	6900 - 8300
	(1950 - 2400)	(1000 - 1200)
Die Melt Temperature - °C	117 – 123	130 - 160
Die Pressure - kPa (psi)	5400 - 6600	5500 - 8000
	(790 - 950)	(800 - 1150)
Line Speed - m/hr (ft/min)	108 - 168	90 - 80
	(5.9 - 9.2)	(5 - 10)
Die Gap - mm	0.6 - 0.8	2 ·
Vacuum – kPa (inch Hg)	0 - 3.4	Atmosphere
	(0 to 16)	

Example 1

Polystyrene foams were prepared both with (7347) and without (7346) a 2.5% nano-particle loading using an LMP extruder. The nano-particle used to prepare this Example was an organoclay, specifically grade Nano-MMT 20A from Southern Clay Products Inc., that was melt compounded with a polystyrene polymer, specifically grade CX5197 from AtoFina, to form a melt polymer. The nano-particles exhibited an intercalated nano-MMT layer structure when examined using X-ray diffraction. The comparison sample did not include any nano-particles, but incorporated 0.8% talc loading as the nucleating agent. The comparison sample exhibited an average cell size of around 186 microns while the exemplary example utilizing the nano-particle foam exhibited a significantly reduced average cell size of around 60 microns. The exemplary example also exhibited a cell wall thickness of around 0.5 micron, and a strut effective diameter of around 5 microns. As reflected below in Table 2, the exemplary foam composition did not exhibit corrugation, was processed without undue process difficulty and provided improvements in compressive strength of around 30%.

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Table 2

Sample	Nano- Particle (Wt.%)	Average Cell (micron)	Cell Anisotropic Ratio*	Density (kg/m ³⁾	Strength (kPa)	Thickness (mm)
7346	0	186	0.949	29.28	286	37
7347	2.5	62	0.968	32	372	26

* Cell anisotropic ratio: $K = z/(x.y.z)^{1/3}$ where, x, an average cell size in the longitudinal (extruding) direction, y, cell size in the transverse direction, and z, cell size in the board thickness direction

Example 2

Sample foams (7349) were produced according to the process outlined in Example 1, but using 0.5% of an intercalated nano-MMT in a polystyrene composition to produce an exemplary foam having a density of about 26.5 kg/m³, a thickness of about 38 mm and a width of about 600 mm. The reduction in the amount of nano-MMT incorporated into the composition resulted in a slightly increased cell size, about 83 microns (FIG. 3), compared with Example 1, while maintaining improved strength, 329 kPa, over the comparative foam compositions.

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Example 3

Foams (7790) were prepared using a nano-particle loading of 2% nano-calcium carbonate from Ampacet, along with 1% tale as an additional nucleating agent and 1% of stabilized hexabromocyclododecone as fire retardant agent in a LMP extruder. The nano-calcium carbonate particles were typically elongated, having average dimensions of 80 nm x 2 μ m, and were provided in a 50% master batch composition in combination with an olefinic copolymer carrier resin. The rest of formulation was polystyrene: 80% Nova 1220 (Melt Index = 1.45) and 16% Nova 3900 (Melt Index = 34.5). The exemplary foam produced was 28 mm thick, 400 mm wide and had an average cell size of 230 microns with a cell orientation – the ratio of the cell dimension in the extrusion direction to the cell dimension in the thickness direction (x/z) – as high as 1.54 (see FIG. 4).

Example 4

Foams (7789) were produced as in Example 3, but used 3.3% intercalated expanded nano-graphite from Superior Graphite Company as the nano-particles. The nano-expanded graphite included nano-sheets of graphite having thicknesses ranging from

about 10 to about 100 nm and widths of around 3 μm. The exemplary foam exhibited substantially the same thickness, width, and density (49 kg/m³) as Example 3, but had a smaller average cell size of 166 microns and cell orientation value of 1.21 (see FIG. 5). The thermal conductivity of this foam is as low as 0.14 K.m²/W for samples after being aged for 20 days.

Example 5

Foams (7289, 7291) were prepared using a Leistritz extruder to produce samples having a thickness of around 10 mm, a width of around 50 mm, and a density of around 46 kg/m³. Both samples with 0.5% of talc as nucleating agent, and 10% of HCFC142b/22 as blowing agent. Some characters of cell morphology are summarized as Table 3:

Table 3

Sample	Nano-	Ayerage	· Cell	C	ell Siz	ze	Cell Wall	Strut
	Particle*	Cell	Orientation				Thickness	Effective
é	(Wt.%)	(micron)	(x/z)				(micron)	Diameter
				х	у	Z		(micron)
7289	0	341	0.99	355	359	339	1.8	4.2
7291	5	174	0.95	165	183	173	0.8	5.1

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Example 6

Foams (7293, 7294) were prepared as in Example 5, but using 6 wt% of carbon dioxide as the blowing agent and 0.2 wt% of talc as a conventional nucleating agent. Some characteristics of the resulting cell morphologies (FIG. 6) are summarized below in Table 4:

Table 4

Samp	le Nano- Particle* (Wt.%)	Average Cell (micron)	Orientation		Cell Siz	ze	Cell Wall Thickness (micron)	Strut Effective Diameter
	-			Х	У.	2.		(micron)
7293	0	380	0.92	355	396	388	1.4	3
7294	. 5	146.	0.76	146	121	158	0.3	5.4

While exemplary embodiments of the process of the present invention have been described with reference to specific details and parameters, those of ordinary skill in the art will appreciate the disclosed process encompasses a variety of components and operating conditions that may be customized to produce a range of manufacturing processes and foam compositions that can be tailored to achieve a desired foam composition properties or adapted to a particular manufacturer's equipment without departing from the spirit and scope of the present invention as defined in the following claims.

WHAT IS CLAIMED IS:

 A method of manufacturing a rigid foam comprising: preparing a polymer melt;

incorporating nano-particles into the polymer melt;

incorporating a blowing agent into the polymer melt under a first pressure and at a first temperature;

extruding the polymer melt under a second pressure and at a second temperature, the second pressure and second temperature being sufficient to allow the polymer melt to expand and form a foam; and

cooling the foam to form a foam product having an average cell size, a cell size distribution, an average cell wall thickness, an average cell strut diameter, a cell orientation, a thermal conductivity, a foam density and a foam strength.

- 2. A method of manufacturing a rigid foam according to claim 1, wherein the polymer includes a major portion of at least one alkenyl aromatic polymer selected from a group consisting of alkenyl aromatic homopolymers, copolymers of alkenyl aromatic compounds and copolymerizable ethylenically unsaturated comonomers.
- 3. A method of manufacturing a rigid foam according to claim 2, wherein: the polymer includes a major portion of at least one alkenyl aromatic polymer selected from a group consisting of the polymerization products of styrene, α-methylstyrene, chlorostyrene, bromostyrene, ethylstyrene, vinyl benzene, and vinyl toluene; and

a minor portions of a non-alkenyl aromatic polymer.

- 4. A method of manufacturing a rigid foam according to claim 3, wherein the polymer includes at least 80 wt% polystyrene.
- 5. A method of manufacturing a rigid foam according to claim 2, wherein the blowing agent includes at least one composition selected from a group consisting of aliphatic hydrocarbons having 1-9 carbon atoms, halogenated aliphatic hydrocarbons having 1-4 carbon atoms, carbon dioxide, nitrogen, water, azodicarbonamide and ptoluenesulfonyl.
- 6. A method of manufacturing a rigid foam according to claim 5, wherein the blowing agent includes at least one composition selected from a group consisting of methane, methanol, ethane, ethanol, propane, propanol, n-butane and isopentane, carbon

dioxide, nitrogen, water, azodicarbonamide, p-toluenesulfonyl, HCFC-142b and HCFC-134a.

- 7. A method of manufacturing a rigid foam according to claim 2, further comprising incorporating an additive into the polymer melt before forming the foam.
- 8. A method of manufacturing a rigid foam according to claim 7, wherein the additive includes at least one composition selected from a group consisting of flame retardants, mold release agents, pigments and fillers.
- 9. A method of manufacturing a rigid foam according to claim 2, wherein the nano-particles have a minimum dimension of less than about 100 nm and are selected from a group consisting of calcium carbonate, intercalated clays, intercalated graphites, exfoliated clays and expanded graphites.
- 10. A method of manufacturing a rigid foam according to claim 9, wherein the nanoparticles are incorporated into the polymer melt at a rate of between 0.01 and 10 weight percent, based on polymer weight.
- 11. A method of manufacturing a rigid foam according to claim 9, wherein the nanoparticles are incorporated into the polymer melt at a rate of between 0.5 and 5 weight percent, based on polymer weight.
- 12. A method of manufacturing a rigid foam according to claim 11, wherein: the nano-particles include a major portion of nano-Montmorillonite (MMT); and the polymer includes a major portion of polystyrene (PS), polyethylene (PE) or polymethyl methacrylate (PMMA).
- 13. A method of manufacturing a rigid foam according to claim 10, wherein the nanoparticles are formed by a technique selected from a group consisting of intercalation with polystyrene, in-situ polymerization of polystyrene (PS) or polymethyl methacrylate (PMMA) with a surface modified nano-Montmorillonite (MMT), and exfoliation of expandable graphite particles in a polystyrene or polymethyl methacrylate matrix.
- 14. A method of manufacturing a rigid foam according to claim 2, wherein: the average cell size is less than about 500 μm; the average cell wall thickness is less than about 10 μm; the average strut diameter is less than about 20 μm; the cell orientation is between about 0.5 and 2.0; and the foam density is less than about 100 kg/m³.

15. A method of manufacturing a rigid foam according to claim 14, wherein: the average cell size is between about 60 and about 120 μ m; the average cell wall thickness is between about 0.2 and about 1.0 μ m; the average strut diameter is between about 4 and about 8 μ m; the cell orientation is between about 1.0 and about 1.5; and the foam density is between about 20 and about 50 kg/m³.

- 16. A method of manufacturing a rigid foam according to claim 2, further comprising incorporating a conventional nucleation agent into the polymer melt at a rate of less than about 2 weight percent based on polymer weight.
- 17. A method of manufacturing a rigid foam according to claim 16, wherein the cell size distribution is bimodal, with a first peak centered between about 50 μ m and 120 μ m and a second peak centered above 200 μ m.
- 18. A rigid foam comprising:

at least about 80 weight percent of a polymer matrix including a major portion of at least one alkenyl aromatic polymer selected from a group consisting of alkenyl aromatic homopolymers, copolymers of alkenyl aromatic compounds and copolymerizable ethylenically unsaturated comonomers; and

less than about 10 weight percent nano-particles having a minimum dimension of less than about 100 nm;

the polymer matrix being further characterized by an average cell size of between about 60 and about 120 μm ; an average cell wall thickness of between about 0.2 and about 1.0 μm ; an average strut diameter of between about 4 and about 8 μm ; a cell orientation is between about 1.0 and about 1.5; and a foam density of between about 20 and about 50 kg/m³.

- 19. A rigid foam according to claim 18, wherein: the polymer matrix is further characterized by a foam compressive strength of at least 300 kPa according to ASTM D1621.
- 20. A rigid polymer foam according to claim 18, wherein: the cell orientation is at least 1.2; and further wherein at least 90 % of the cells are closed cells.

FIG. 1
Exemplary Extruded Polystyrene Foam

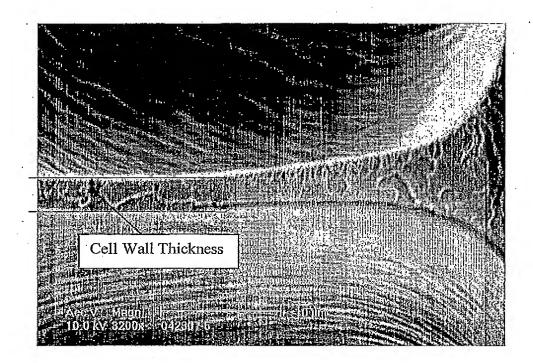


FIG. 2
Exemplary Extruded Polystyrene Foam

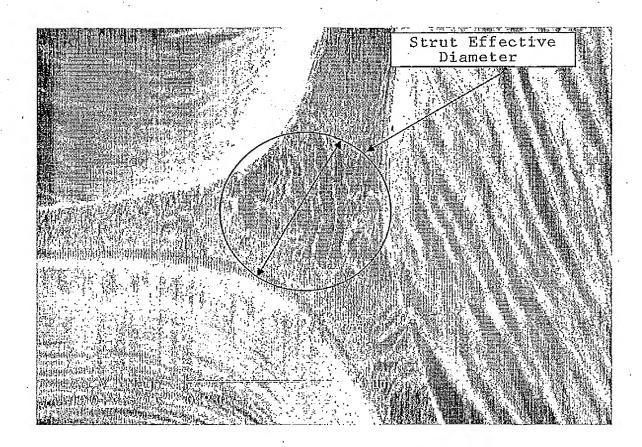


FIG. 3

Exemplary Extruded Polystyrene Foam with 2.5% Nano-MMT

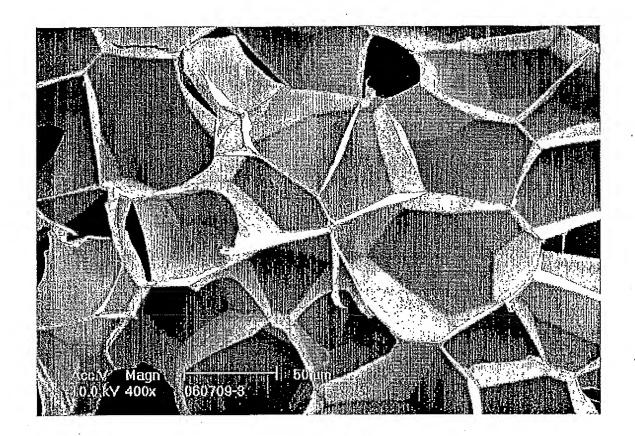


FIG. 4

Exemplary Extruded Polystyrene Foam with Nano-Calcium Carbonate

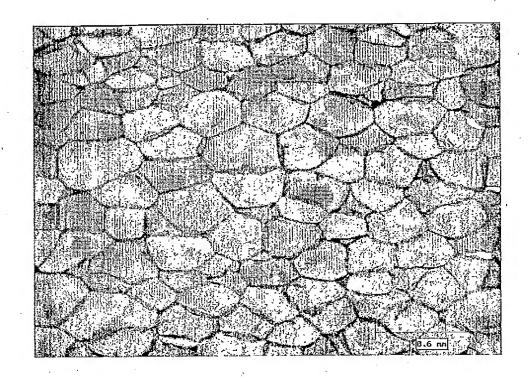


FIG. 5

Exemplary Extruded Polystyrene Foam with Nano-Expanded Graphite

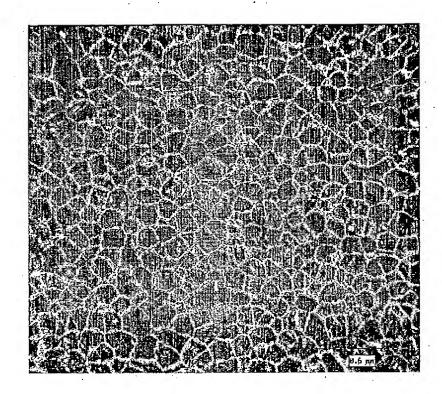
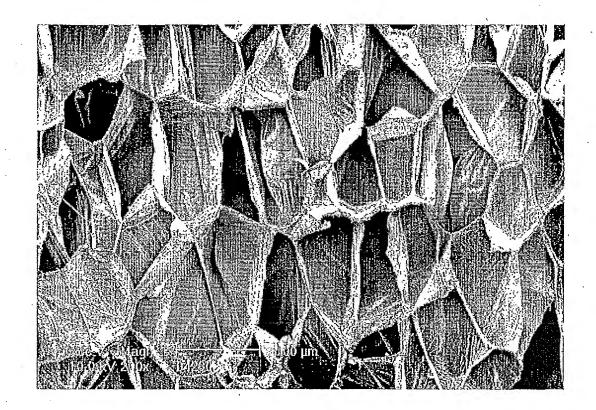


FIG. 6 Exemplary Extruded Polystyrene Foam with 5% nano-MMT and 6% $\rm CO_2$



INTERNATIONAL SEARCH REPORT

Inter al Application No PCT/US2004/039336

A CLASS	BOATION OF CHE LECT MATTER		
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C. DOCUM	ENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the refe	evant passages	Relevant to claim No.
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4	March 2005	07/04/2005	**
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